Wednesday, May 13
Facility-specific Workshops

APS/CNM Workshop 7
Experimental and Computational Challenges of *in situ* Multimodal Imaging of Energy Materials

Location: Bldg. 401, Room A1100

Organizers: Yuzi Liu (CNM), Yang Ren (APS), Maria Chan (CNM), and Xianghui Xiao (APS)

Real-time imaging, scattering, and spectroscopy are primary experimental techniques to probe the dynamic process of materials formation, evolution, and structure-property relationships in energy materials.

In recent years, transmission electron microscopy (TEM) and synchrotron-based x-ray methods have been further developed to incorporate new environments and detectors to meet fast-growing research needs in energy materials science. Scientists have applied these techniques to investigate myriad processes, such as nanoparticle nucleation and growth and phase transitions of energy storage materials during the charge and discharge cycling. For example, *in situ* TEM provides a platform to study materials nucleation, growth, and electrochemically driven growth of dendrites on lithium anodes at the atomic scale.

In addition, the improvements in synchrotron x-ray optics and high-brightness coherent light sources allow investigation of phase changes and other chemical transformations with high spatial and temporal resolution.

Both electron and x-ray imaging methods provide opportunities to study energy materials in three-dimensional views, in addition to providing spectroscopic information.

Integration of these different techniques to study the energy materials in multimodal approaches at different length scales and temporal scales will help scientists further understand the working mechanisms of energy materials.

High-performance computation is crucial for the deployment of such multimodal imaging capabilities, both in the form of high-volume and high-speed data acquisition and processing and in the form of data interpretation via atomistic and first-principles simulations. The coupling of the experimental and computational development requires integrated teams and multidisciplinary efforts. Argonne National Laboratory has established the Integrated Imaging Initiative to emphasize the importance of multimodal imaging.

This workshop will cover the most recent developments and applications of *in situ* characterization techniques and high-performance computations for the study of energy materials. Particular attention will be paid to *in situ* multimodal imaging in the investigation of phase transformations, dynamics, crystal growth, crystal defect formation and elimination, chemical reactions, and interface dynamics in environmental conditions. The goal of this workshop is to provide a forum for experimental and computational scientists and facility users from various fields who are utilizing *in situ* methods to understand the structure, physics, and chemistry of energy materials.

8:30 – 8:40 Opening Remarks

8:40 – 9:30 Nigel Browning (Pacific Northwest National Laboratory)
Quantitative in situ *Transmission Electron Microscopy*

9:30 – 10:00	Haimei Zheng (Lawrence Berkeley National Laboratory) *Real-time Imaging of Materials Transformations in Liquids*
10:00 – 10:35	Break
10:35 – 11:05	Chongmin Wang (Pacific Northwest National Laboratory) In situ *and* ex situ *TEM Study of Anode and Cathode for Lithium-ion Battery and Beyond*
11:05 – 11:35	Scott Warren (University of North Carolina at Chapel Hill) *Identifying Champion Nanostructures with Electron, Light, and Force Microscopies*
11:35 – 12:00	Jeffrey Greeley (Purdue University) *Computational Investigations of Interfacial Structure and Reactivity*
12:00 – 1:30	Lunch
1:30 – 2:20	Paul Fenter (Argonne National Laboratory) In situ *Studies of Structures and Processes at Model Electrode/Electrolyte Interfaces*
2:20 – 2:50	Jiajun Wang (Brookhaven National Laboratory) In situ *2D/3D Imaging of Battery Materials with Full-field Transmission X-ray Microscopy*
2:50 – 3:20	Break
3:20 – 3:50	Raymond Osborn (Argonne National Laboratory) *Single Crystal Diffuse Scattering: Big Data beyond the Workflow*
3:50 – 4:20	Todd Turner (Air Force Research Laboratory) *Microstructural Modeling of a Combined High-energy Diffraction Microscopy Experiment*
4:20 – 4:50	Mark Hereld (Argonne National Laboratory) *An Integrated Platform for Studying Complex Biological Systems*
4:50	Closing Remarks

WK7

Quantitative *in situ* Transmission Electron Microscopy

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Many processes in materials science, chemistry and biology take place in a liquid environment — such as the synthesis of nanoparticles, biological cellular functions and the operation of Li-ion/next generation batteries. In these cases, the overall process/function of the system is a result of a series of complicated transients, where a change in the order, magnitude or location of any of the individual steps can lead to a radically different result. Understanding

and subsequently controlling the final system outcome can therefore be greatly aided by the ability to directly observe these fundamental transient processes as and where they happen. Aberration corrected (scanning) transmission electron microscopy [(S)TEM] has the spatial resolution (typically < 0.1 nm) to directly visualize the atomic scale structural and chemical variations taking place in materials. Historically, such high resolution microscopy has been used to analyze materials before and after a process takes place to infer the dynamics of what happened in between. While there are still great advances that can be made with such analyses (at the very least in providing benchmark structures for nanoscale systems), a major breakthrough in recent years has been the design and implementation of *in situ* gas and liquid stages that allow (S)TEM images to be obtained while the transient processes are actually taking place. Performing experiments using these *in situ* stages presents numerous challenges to the traditional means of analyzing samples in an electron microscope — we are now dealing with the variability of dynamic process rather than a more straightforward static structure. In this presentation, I will discuss the recent developments in the design and implementation of *in situ* stages being pursued at the Pacific Northwest National Laboratory (PNNL) that permit quantitative information to be extracted from the observations. Examples of the use of these capabilities for the direct imaging of the fundamental processes important for energy storage and conversion materials will be presented. As the *in situ* stages have been designed to be incorporated into both high spatial resolution aberration corrected (S)TEM and high temporal resolution Dynamic TEM (DTEM), the potential for future experiments to study fast dynamics, including those involving live biological structures, will also be discussed.

This work was supported in part by the Joint Center for Energy Storage Research (JCESR), an Energy Innovation Hub funded by the Department of Energy, Office of Science, Basic Energy Sciences. The development of the stages was supported by the Chemical Imaging Initiative, a Laboratory Directed Research and Development Program at Pacific Northwest National Laboratory (PNNL). PNNL is a multi-program national laboratory operated by Battelle for the U.S. Department of Energy (DOE) under Contract DE-AC05-76RL01830. A portion of the research was performed using the Environmental Molecular Sciences Laboratory (EMSL), a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at PNNL.

WK7

Real-time Imaging of Materials Transformations in Liquids

Haimei Zheng

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An understanding of how materials grow and transform in their working environment is essential to the development of functional materials and efficient devices for energy applications. We study the growth and transformation of materials in liquids by the development and application of liquid cell transmission electron microcopy (TEM). In this talk, I will present our study of shape evolution mechanisms of colloidal nanoparticles using liquid cell TEM. There have been a lot of studies on controlling shape of nanoparticles since the catalytic or other surface-enhanced properties of the nanocatalysts are highly dependent on their shape. However, how facets develop during nanoparticle growth is largely unknown due to the lack of direct observation. Using *in situ* liquid cell TEM, we have been able to identify unique growth mechanisms and have discovered rules that are applied to bulk systems break down at the nanoscale. At the end, I will also briefly show our development of electrochemical liquid cells for the study of dissolution-deposition at the electrode-electrolyte interfaces in battery applications.

WK7

In situ and *ex situ* TEM Study of Anode and Cathode for Lithium-ion Battery and Beyond

Chong-Min Wang

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Over the last decades, we have witnessed tremendous progress on the development of aberration corrected transmission electron microscopy and scanning transmission electron microscopy. As a result of this development, imaging of materials at atomic scale and spectroscopying at sub-nanometer scale become a routine practice. The

questions now come to how we extend the microscopy and spectroscopy methodologies to analyze materials at or near realistic/operating condition, typically such as real-time observation of catalytic process, oxidation and reduction, bio-tissue in a liquid cell, defects generation and interaction under deformation conditions, mass transport and microstructural evolution, charge and ion transport process in electrochemical cells. In this presentation, I will focus on *in situ* TEM techniques that developed for probing into the structural and chemical information of energy storage materials. *In situ* high-resolution imaging enables direct observation of structural evolution, phase transformation and their correlation with mass, charge and electron transport, which provide insights as how active materials failure with cyclic charging and discharging of a battery. In perspective, challenges and possible direction for further development of the *in situ* TEM imaging and spectroscopic methods for energy storage materials and other field will also be discussed.

WK7

Identifying Champion Nanostructures with Electron, Light, and Force Microscopies

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Assemblies of 0D, 1D, and 2D materials have emerged as one of the most important architectures for solar cells, fuel cells, batteries, and water-splitting devices. The complexity of these materials, as exemplified by the huge number of unique interfaces, has frustrated attempts to identify the relationships between structure and electronic properties, a knowledge of which are crucial for improving device performance. I describe the development of several techniques and instruments based on electron, light, and force microscopies that allow *ex situ* and *in situ* imaging of single nanostructures with a spatial resolution that is often below 2 nm. This presentation will focus on our recent efforts to correlate structure and properties in aggregates of nanoparticles that are of interest in solar water splitting. By performing correlations on statistically significant sample sizes, we are able to deduce how specific types of nanoparticle interfaces result in high performance in water splitting, ultimately allowing us to design macroscopic devices with record ("champion") performance. We will briefly describe how new microscopy techniques and instruments are allowing this approach to be generalized to new material systems.

WK7

Computational Investigations of Interfacial Structure and Reactivity

Jeff Greeley

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Advances in the theoretical understanding of interfacial electrocatalysis have, over the past decade, permitted the extension of periodic Density Functional Theory studies, which have traditionally been applied to probe chemistry at gas/solid interfaces, to electrochemical systems where potential-dependent reactions occur at liquid/solid interfaces. Indeed, such techniques have been employed to study a surprisingly wide class of chemical processes, ranging from electrochemical oxygen reduction to carbon dioxide reduction to water splitting. In this talk, I will briefly review the application of these simple techniques to the classic case of the hydrogen evolution reaction on transition metal alloys. Next, I will demonstrate how very similar approaches can be applied to understand certain aspects of reactivity at bifunctional oxide/metal interfaces, and I will close by drawing analogies between these electrocatalytic processes and traditional heterogeneous catalytic chemistries at metal/support interfaces.

WK7

In situ Studies of Structures and Processes at Model Electrode/Electrolyte Interfaces

Paul Fenter

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Understanding and controlling reactions within electrochemical energy storage systems is a significant scientific and technical challenge. This is due to the complexity of these systems (e.g., for both the solids and electrolytes), as well as the extreme environments and significant structural and chemical changes that can take place as a function of applied potential. The behavior at the solid-electrolyte interface itself is especially poorly understood. I will review our recent work in which we seek to isolate and understand the role of interfacial reactivity in these systems through *in situ*, real-time, observations of electrochemically driven reactions. This is achieved by observing well-defined model electrode-electrolyte interfaces using x-ray reflectivity. I will discuss two distinct types of electrochemical energy storage systems: 1) lithium ion battery chemistries in which energy is stored by lithium ion insertion into electrodes (e.g., Si, Si_xCr, Ge, NiO). The goal of this work is to control the complex lithiation reaction path of these conversion reactions through the use of thin-film and multilayer electrode structures; and 2) super-capacitor systems, in which energy is stored by surface adsorption. For these systems, we are studying the static structures and dynamical response of room temperature ionic liquids at potential-controlled carbon interfaces which we find have inherently slow dynamics associated with the reorganization of the interfacial RTIL structure.

This work was supported as part of the Center for Electrochemical Energy Science (CEES) and the Fluid Interface Reactivity Structure and Transport Center (FIRST), which are Energy Frontier Research Centers funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences. The work was done in collaboration with T. Fister, S.S. Lee, A. Uysal, H. Zhou (ANL), J. Esbenshade, B. Long, A. Gewirth (UIUC), X. Chen, G. Evmenenko, M. Bedzyk (Northwestern), G. Feng, S. Li, P. Cummings (Vanderbilt), S. Dai (ORNL), and Y. Gogotsi (Drexel).

WK7

In situ 2D/3D Imaging of Battery Materials with Full-field Transmission X-ray Microscopy

Jiajun Wang and Jun Wang

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Electrochemically driven phase transformation directly influences electrode performance in lithium ion batteries. Advancing our understanding of the mechanism necessitates the development of advanced tools with *in situ* capability to track the dynamic phase and structural changes of battery materials at 2D and 3D. The synchrotron hard x-ray imaging technique is particularly interesting for applications in battery studies because of its natural characteristics: it is non-destructive, chemically and elementally sensitive, environmentally friendly, and highly penetrative to enable *in situ* study of a real battery[1–3]. Considerable progress in this field has been reported recently from our group, beamline X8C at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL), where a new full-field hard x-ray imaging technique, transmission x-ray microscopy (TXM), has been developed and applied to battery microstructure study [4,5]. In this talk, we will present our recent work using *in situ*/*in operando* TXM approach to track phase transformation at 2D and 3D for anode (Tin) and cathode ($LiFePO_4$) battery materials [1–3]. Challenges and opportunities of TXM technology for energy materials research will be also discussed. This *in situ* imaging approach has a wide variety of applications in other fields, such as fuel cells, catalysis, environmental science and biological science.

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WK7

Single Crystal Diffuse Scattering: Big Data beyond the Workflow

Raymond Osborn

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Single crystal diffuse x-ray scattering is a three-dimensional probe of complex defect structures embedded in an otherwise perfect lattice, providing insight into the role of disorder in generating materials properties such as fast-ion conduction or relaxor ferroelectricity. With the new generation of fast area detectors, full three-dimensional volumes of reciprocal space can be generated using continuous sample rotations, with several thousand images collected in less than 10 minutes. We have been developing methods of handling data collected at rates of several GB per minute by streaming images to a data server, combining the frames in NeXus files that contain comprehensive experimental metadata, and transforming the arrays into reciprocal space for real-time inspection and manipulation. A collaboration with Argonne computational scientists is developing interactive tools for the data analysis of very large (10–50GB) remote data sets using resources such as Globus catalogs and the Swift parallel scripting language to enable flexible script-based approaches to 'playing' with the data once the basic data reduction workflow is complete. These tools are being written in a sufficiently general way that they may be useful in other scientific domains.

WK7

Microstructural Modeling of a Combined High-energy Diffraction Microscopy Experiment

Todd Turner

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The strategic development of new engineering materials with improved performance rests upon establishing computational models that link materials processing, microstructure, and properties/performance. However, validating micro mechanical models that capture the relevant deformation at the microstructural level has remained elusive without access to experimental data at the relevant grain-level scale. Emerging experimental techniques such as High Energy x-ray Diffraction Microscopy (HEDM) address a critical need with respect to validation experiments for models focused on the prediction of mechanical properties at the mesoscale, where the response of grains and similar microstructural features are explicitly tracked. This presentation will focus on work done at the 1-ID beamline at the Advanced Photon Source, where grain level morphology and elastic strain evolution were tracked through HEDM techniques. A crystal plasticity finite element model based on this experiment will be presented, and the results of the model will be compared to the experimentally obtained HEDM data.

WK7

An Integrated Platform for Studying Complex Biological Systems

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Imaging is one of the most important and powerful methods yet devised to learn about the world around us. In the Small Worlds project, an interdisciplinary team of scientists at Argonne, University of Chicago, and Northwestern University are developing a new multi-modal imaging capability for studying complex multi-agent processes in cells and systems of cells across spatial and temporal scales. This experimental platform is composed of integrated hardware, software, and molecular-scale reporters that will enable the study of systems biology problems involving many parts and spanning spatial scales from the nanometer to the millimeter and temporal scales from subseconds to days.

We have begun to develop and integrate three imaging methods that, when used together, will lead to tremendous new understanding of the organization and dynamic function of a wide range of complex biological systems. The first approach, scanning *x*-ray fluorescence (XRF) imaging, allows sub-micron scale measurements of intact complex systems in their native environment, even if that environment is opaque to visible light. The second method, correlative electron-optical imaging, allows ultra-resolution imaging of whole organisms by transmission electron microscopy (TEM) and 3D spatial correlation with optical imaging of the identical (fixed) samples. The third proposed development, the novel 3D snapshot interferometric holographic microscope (3D-SIHM), is optical 3D microscopy of dynamic living systems with nanoscale resolution by interferometry, plus multi-scale volumetric imaging by holography in a "snapshot" mode for quantitative determination of transport on nanometer to 100 μm scales. The three approaches are synergistic when used in tandem with reporters that function across one or more of the imaging methods.

The contingent of capabilities developed in this project will enable construction of dynamic experiments that can track and correlate interrelated molecular actors in complex processes, while providing detailed corroboration and supplementary data across physical scales with qualitatively different imaging modalities.